

L095.960



PATENT SPECIFICATION

NO DRAWINGS

L095.960

Date of Application and filing Complete Specification: Oct. 20, 1966.

No. 46919/66.

Application made in United States of America (No. 502,395) on Oct. 22, 1965.

Complete Specification Published: Dec. 20, 1967.

© Crown Copyright 1967.

Index at acceptance:—C3 P12; C3 R(1C6, 1C7, 1C8, 1C9, 1C11, 1C12, 1C13, 20C6, 20C7, 20C8, 20C9, 20C11, 20C12, 20C13)

Int. Cl.:—C 08 f 43/06

COMPLETE SPECIFICATION

Sealing Compositions

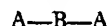
We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns new sealing compositions containing block copolymers as an elastomeric component.

Compositions for sealing cracks and other openings such as joints are commonly prepared by compounding a drying oil such as linseed oil with a filler such as clay or talc to form a putty which can be pressed or forced into cracks.

The deficiencies of the well-known putties of the past became increasingly apparent when used in curtain wall construction, since these traditional compounds did not fulfil the new requirements of tensile strength, elongation, elastic recovery, adhesion and long term dependability. As a result, modern sealants have been developed which are usually high solids elastomeric adhesives. Many of the common elastomers have been used as sealant vehicles which may be divided into two types, namely, those that develop elastomeric properties by "curing" through solvent evaporation and, secondly, those that develop elastomeric properties through a chemical reaction such as cross-linking or polymerization. While chemically curing sealants of the recent past have usually had the best performance, they are also the most expensive. The solvent type of sealants which have been recently developed may be inexpensive, but they are generally lacking in certain areas of performance.

In accordance with the present invention, there is provided a sealing composition which comprises a block copolymer having the general formula



in which each A is an independently selected polymer block of a vinyl substituted aromatic hydrocarbon having an average molecular weight in the range 8,000 to 45,000 and B is a polymer block of a conjugated diene having an average molecular weight in the range 35,000 to 150,000, or a hydrogenated derivative thereof, together with, based on 100 parts by weight of the said copolymer,

- (a) 75 to 200 parts by weight of a liquid hydrocarbon boiling between 100°C and 175°C;
- (b) 50 to 175 parts by weight of a resin selected from hydrogenated rosin, terpene resins, polymerized rosin, pentaerythritol esters of rosin, polyalkenes and mixtures thereof;
- (c) 15 to 50 parts by weight of an alkylated di or polymethylol phenolformaldehyde resin;
- (d) 150 to 400 parts by weight of a filler selected from alkaline earth metal carbonates, oxides and clays having average particle diameters between 5 and 75 microns;
- (e) 10 to 300 parts by weight of a filler selected from silicas, alkaline earth metal

oxides and carbonates having average particle diameters between 0.005 and 1 micron; and
(f) 0 to 50 parts by weight of a mineral oil.

Two preferred species of the block copolymers forming the elastomeric component of the composition have the block configuration polystyrene-polybutadiene-polystyrene and polystyrene-polyisoprene-polystyrene and hydrogenated derivatives thereof. The hydrogenated derivative of the second of the above defined block copolymers is of especial interest, not only because of its high stability but because of the elastomeric nature of the hydrogenated mid-section which resembles that of an ethylene-propylene rubber while the end blocks either remain as polymer blocks of a vinyl substituted aromatic hydrocarbon or if hydrogenated become saturated blocks typified by vinyl cyclohexane polymer blocks. Thus, the fully hydrogenated preferred species has the block configuration polyvinylcyclohexane-[ethylene-propylene]copolymer-polyvinylcyclohexane.

These particular block copolymers attain the stress-strain properties of an elastomer without curing or vulcanization. Thus, they are sharply differentiated from other rubbers such as natural rubber, polybutadiene, and SBR which require vulcanization in order to attain satisfactory stress-strain properties. Consequently, the sealant compositions of the present invention represent a hybrid between the two general types of elastomeric caking compounds heretofore developed in that it "cures" by solvent evaporation but does not require vulcanization or chemical cross-linking such as is necessary with the polyurethanes.

The compositions of the invention may function satisfactorily without any mineral oil extender but it has been found that the oil functions in an unexpected manner not only to plasticize, soften and tackify the composition but also creates a consistency especially suitable for rapid escape of the volatile solvent utilized for viscosity purposes. On the other hand, the proportion of oil which may be incorporated is strictly limited, since if proportions in excess of 50 phr (parts by weight per hundred parts by weight of block copolymer) are used, then poor adhesion to the surfaces being sealed results.

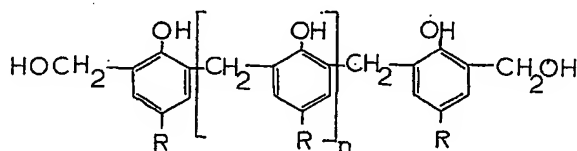
The type of mineral oil utilized for this purpose is not especially critical but should be one which does not volatilize under the conditions of service. Consequently, it is preferred that it has a boiling point above about 550°F and a viscosity between about 40 and 250 SSU at 210°F. Such oils are often referred to as "processing and rubber extending oils" and have aromatic contents varying from about 10% to about 50%.

One of the important components of the composition may be regarded as a "temporary" component in that it is a relatively volatile liquid hydrocarbon of such a character that the other components may be thinned thereby but from which it will readily escape over a period of about several weeks after application of the sealant into its service position. Consequently, it is necessary that the liquid hydrocarbon boils between about 100°C and 175°C. Such hydrocarbons are especially typified by toluene, xylene and mixtures of hydrocarbons boiling within this general range, often referred to as "mineral spirits". If the boiling range is below the minimum specified, the solvent is released too rapidly and surface hardening of the remaining components may occur before the sealant is properly levelled into position. On the other hand, if the boiling range is extended beyond that specified then it is too slow to release properly and the composition may be subject to flow or sagging, especially when it is placed in a vertical position.

One of the major components of the composition under consideration comprises a resin. It was found that ordinary phenolformaldehyde resins were not compatible with the block copolymers. Polymerized petroleum hydrocarbons were also unsatisfactory but terpene polymers were found to be adequate as were polymerized rosin and hydrogenated rosin together with pentaerythritol esters of rosin and polyalkenes. The most desirable class of materials comprised the hydrogenated rosins (either gum rosin or wood rosin) which result in increased elongation of the compositions under consideration. Furthermore, the saturated nature of the hydrogenated rosins make them highly resistant to oxidation, discoloration and changes in solubility characteristics when exposed to air and sunlight.

While all of these factors are satisfied by the particular class of resinous materials described immediately above, it was found in the course of developing the compositions of this invention that if these resins were the sole resinous component the compositions were lacking in one essential respect, namely, in adhesion to the surfaces being sealed. Sealant adhesion to surfaces is a stringent requirement and usually the most difficult

to meet. It has been noted hereinbefore that the oil content is critical in this respect and was therefore restricted to the recited range of 0—50 phr. Even when so restricted, however, the resulting compositions containing only the one resin of the class given hereinbefore did not exhibit proper adhesion. Consequently, some enhancement of adhesion was required by a further modification of the composition. This was found in the use of a critically limited amount of alkylated di or polymethylol phenol-formaldehyde resins. The use of this class of oil-soluble resins was investigated over much wider concentration ranges. However, it was noted that when proportions larger than those specified (15—50 phr) were employed the resulting compositions including the block copolymer exhibited poor physical properties indicative of incompatibility. However, when utilized within the restricted range specified there was a dramatic increase in sealant adhesion to all types of surfaces investigated. Certain of the alkylated dimethylol phenol-formaldehyde resins have the general configuration as follows:



in which the groups R represent alkyl radicals having from 4 to 9 carbon atoms each and in which n is an integer of from 1 to 50. They impart the oil solubility required for compatibility in the present system. The average molecular weight of the resins preferably lies between 350 and 1,500 while the methylol content is preferably between about 5 and 20% by weight. While in dimethylol phenol-formaldehyde resins the methylol groups are normally regarded as being situated on the terminal phenolic groups, the methylol content may be increased without molecular weight increase by replacement of one or more of the R alkyl radicals with methylol radicals, such resins having a higher methylol content being denoted herein as alkylates, polymethylol phenol-formaldehyde resins. In alternative alkylated polymethylol phenol-formaldehyde resins methylol radicals may supplement the alkyl radicals instead of replacing them. In the usual commercially available alkylated di or polymethylol resins, the alkyl radicals are believed to be in positions para to the hydroxyl groups of each phenol radical. The preferred resins of this class have softening points (Nagel) of 80—95°C, specific gravities at 25°C of between about 1.02 and 1.04 and acid numbers between about 30 and 40.

In order to be effective commercially, it is necessary for the entire composition to be relatively low in cost, while still maintaining satisfactory physical properties for the sealing requirements as detailed hereinafter. This may be achieved primarily by the use of fillers. It was found that no one filler was satisfactory but, in fact, two fillers were necessary. It was found possible to employ limited amounts in the order of 150—400 parts by weight based on one hundred parts by weight of the block copolymer of fillers comprising alkaline earth metal carbonates, oxides and clays having relatively coarse particle diameters between 5 and 75 microns. However, if large proportions were employed, then the physical properties of the resulting compositions degenerated, particularly insofar as elasticity and cohesive strength were concerned. Therefore, it was necessary to utilize in combination with the relatively coarse filler other fillers having extremely finely divided particles in the order of 0.005 and 1 micron. Depending on the particular filler employed and its particle size, this finely divided filler should be present in amounts between about 10 and 300 phr and may comprise silicas, particularly fumed silicas, metallic oxides and alkaline earth metal carbonates. The fumed silicas are of such fine particle size (in the order of 0.005—0.02) that they are used only in small proportions, up to about 30 phr. However, for that somewhat larger but still small sized alkaline earth metal carbonates and oxides wherein the particle sizes vary from about 0.025 to 1 micron proportions in the order of 150 and 275 phr, may be employed. However, if attempts are made to entirely replace the relatively coarse fillers having a diameter of 5—75 microns with the finer fillers, it is found that the per cent of shrinkage of the entire composition rises sharply and results in unsatisfactory service.

The following table, Table I, gives both the broad range of permissible proportions of each of the essential components and also the preferred range of proportions thereof

TABLE I

Component	Parts By Weight	
	Broad Range	Preferred Range
A Block copolymer	100	100
B Extending oil	0—50	20—35
C Volatile hydrocarbon	75—200	85—125
D Rosin-type resin	50—175	110—155
E Dimethylol phenolic resin	15—50	20—40
F Coarse filler	150—400	175—225
G Fine filler	10—300	150—275

The sealing compositions of the invention satisfy the combination of properties required of a satisfactory sealant. These properties are set out in Table II.

TABLE II
Criteria for an elastomer sealant

5	I. <i>In Use</i>	5
	1. Rheology should allow easy transfer from containers.	
	2. Rheology should be designed for application:	
	— Non sag for vertical joints.	
10	— Self levelling for horizontal joints.	10
	3. Extrusion properties must be satisfactory at all working temperatures.	
	4. Tooling—easily “tooled” to desired surface finish and level.	
	5. Product should not be toxic or have undesirable odour.	
	6. Product should be easily cleaned from tools and surfaces.	
15	II. <i>Performance</i>	15
	1. Excellent adhesion to building surfaces.	
	2. Develop good elastomeric properties.	
	3. Should reach a tack-free state rapidly.	
	4. Exhibit slight shrinkage.	
20	5. Adequate cohesive strength for application—never more than adhesive strength.	20
	6. No colour change.	
	7. No adverse effect over ambient temperature range.	
	8. Not affected by sunlight, water, oxygen, ozone, wind pressure, dirt.	
	9. Good chemical resistance.	
25	10. Non-staining and non-corrosive.	25
	11. Maintain desirable properties over estimated life.	
	12. Performance should comply with applicable specifications.	

In addition to the essential components, other optional materials may be employed for improvement, modification or stabilization of these compositions. For example, antiozonants and antioxidants may be utilized. A preferred class of antioxidants comprise the nickel dialkyldithiocarbamates. Specific compounds in this group include nickel dibutyldithiocarbamate, nickel diamyldithiocarbamate and nickel diisooctyldithiocarbamate. These may be supplemented by the presence of alkylated phenols and their derivatives as well as by aromatic amines. Phenolic antioxidants are especially desirable, of which one of the most effective is the class of trialkyl-substituted tri(alkyl hydroxybenzyl)benzenes. An especially desirable antioxidant within this group is 1,3,5-trimethyl-2,4,6-tri(3,5-di-tertiarybutyl-4-hydroxybenzyl)benzene. These antioxidants and antiozonants are used in the usual additive amounts, namely, between about 0.25% and about 1% each. Colouring materials and masking agents, such as carbon blacks, titania

etc., may be utilized as long as they do not interfere with the effective set of physical properties obtained by the special combination of components discussed above.

EXAMPLE

The physical testing of the subject sealants presents a problem since they are in effect a hybrid between the solvent release type of sealant and the curative sealants. Consequently, the tests such as those detailed by the American Standard's Test A 116.1—1960 apply only when they are modified to take this hybrid character into account. The most realistic type of testing is field testing wherein the sealants are placed in a working position such as in the sealing of curtain wall sections and observed for a period of time.

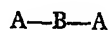
Components *)	Parts by weight	
	Sample A	Sample B
A Polystyrene-polybutadiene-polystyrene block molecular weights 14,000—67,000—14,000	100	100
B Napthenic mineral oil, 53 SSU at 210°F	32	30
C Toluene	105	100
D hydrogenated rosin	145	135
E Tert. butyldimethyl phenol-formaldehyde resin 14%w methylol content	25	35
F Calcium carbonate 25—45 microns average particle size	200	200
G Calcium carbonate 0.05 micron average particle size	250	250

* Order of mixing A; B + C + D + E; F + G.

Sealing of a curtain wall building was effected by filling joints between the concrete slabs with the above sealant A and other joints with sealant B, the joints being about 1/2 inch deep and varying from 1/4 to 3/4 inches in width and 12 feet high. Both sealants had good working and handling properties and did not show evidence of sagging. Periodic inspection after installation showed that the sealants had cured well, i.e., the solvent had evaporated satisfactorily and no shrinkage problems were evident. There was no sign of adhesion failure and all indications showed that the subject building sealant compositions A and B were superior to other solvent-type sealants and unlike most of the latter can be used successfully in moving joint applications in place of the more expensive chemically curing sealants.

WHAT WE CLAIM IS:—

1. A sealing composition which comprises a block copolymer having the general formula



in which each A is an independently selected polymer block of a vinyl substituted aromatic hydrocarbon having an average molecular weight in the range 8,000 to 45,000 and B is a polymer block of a conjugated diene having an average molecular weight in the range 35,000 to 150,000, or a hydrogenated derivative thereof, together with, based on 100 parts by weight of the said copolymer,

(a) 75 to 200 parts by weight of a liquid hydrocarbon boiling between 100°C and 175°C;

- (b) 50 to 175 parts by weight of a resin selected from hydrogenated rosin, terpene resins, polymerized rosin, pentaerythritol esters of rosin, polyalkenes and mixtures thereof;
- 5 (c) 15 to 50 parts by weight of an alkylated di or polymethyl phenolformaldehyde resin; 5
- (d) 150 to 400 parts by weight of a filler selected from alkaline earth metal carbonates, oxides and clays having average particle diameters between 5 and 75 microns;
- (e) 10 to 300 parts by weight of a filler selected from silicas, alkaline earth metal oxides and carbonates having average particle diameters between 0.005 and 1 micron; and 10
- 10 (f) 0 to 50 parts by weight of a mineral oil.
2. A sealing composition as claimed in claim 1, in which in the block copolymer A—B—A, each A is polystyrene.
- 15 3. A sealing composition as claimed in claim 1 or 2, in which in the block copolymer A—B—A, B is polybutadiene. 15
4. A sealing composition as claimed in claim 1 or 2, in which in the block copolymer A—B—A, B is polyisoprene.
5. A sealing composition as claimed in any one of the preceding claims, in which the resin (b) is hydrogenated rosin.
- 20 6. A sealing composition as claimed in any one of the preceding claims, in which the alkylated di or polymethylol phenol-formaldehyde resin (c) has an average molecular weight between 350 and 1,500, has a methylol content between about 5% and 20% by weight and contains alkyl substituents having 4 to 9 carbon atoms each. 20
7. A sealing composition as claimed in any one of the preceding claims, in which the mineral oil has a viscosity of 40 to 250 SSU at 210°F.
- 25 8. A sealing composition as claimed in any one of the preceding claims, in which the liquid hydrocarbon is toluene. 25
9. A sealing composition substantially as hereinbefore described with special reference to the Example.
- 30 10. The use as a sealing agent of a composition as claimed in any one of the preceding claims. 30

WILLENS & ROBBINS,
Chartered Patent Agents,
Shell Centre,
London, S.E.1.
Agents for the Applicants.